Unlocking the fertiliser potential of waste-derived biochar

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Abstract

Mankind is facing a phosphorus (P) crisis. P recycling from anthropogenic waste is critical to close the P loop. Pyrolysis could be the ideal treatment for materials, such as sewage sludge, producing a safe, nutrient-rich biochar product while sequestering the inherent carbon (C). However, pyrolysed sewage sludge typically contains low levels of potassium (K) and plant available P making the material rather unsuitable for use as fertiliser. Here, a novel treatment was investigated to produce an optimised P and K biochar fertiliser. We doped sewage sludge with a low-cost mineral (2 and 5% potassium acetate) and pyrolysed it at 700°C. The percentage water-extractable of the total P content in biochar increased by 237-times with 5% K addition compared to the undoped biochar. After six water-extractions, all the K and 16% of P was obtained. Further optimisation is feasible through adjustments of the biochar pH or doping the feedstock with other forms of K. Using XANES and synchrotron XRF mapping, we identified highly soluble potassium hydrogen phosphate up to 200-300 µm below the biochar surface. This simple and cost-effective modification enables the use of sewage sludge

as safe biochar fertiliser with tailored P availability that also supplies K, improves soil properties and sequesters C.

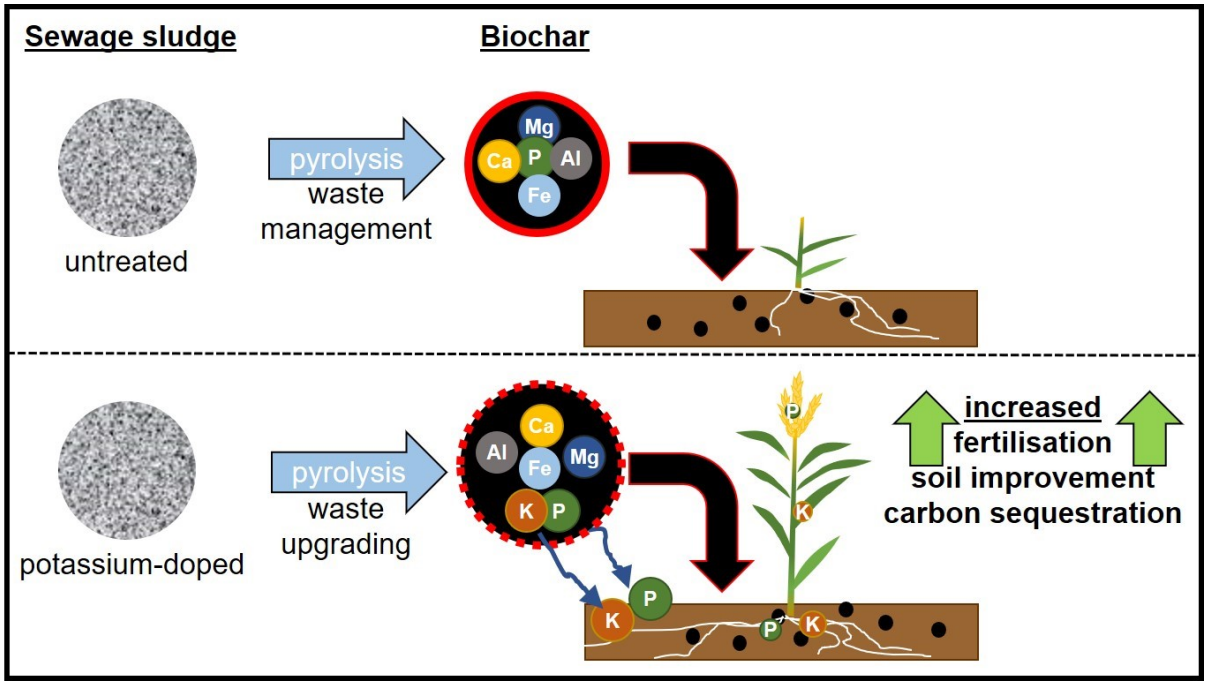
Keywords

Biochar, pyrolysis, sewage sludge, fertilizer, phosphorus, potassium, XANES

Abbreviations

FC, fixed carbon; PTE, potentially toxic element; LCF, linear combination fitting

Graphical Abstract



Synopsis

We demonstrate a technique for the efficient production of a safe and sustainable sewage sludge fertiliser via pyrolysis.

Introduction

Phosphorus (P) is an essential plant nutrient and a vital planetary resource on which global agriculture and food production depends. While nitrogen (N) can be biologically or artificially fixed from air with the help of energy, this is not an option for P, and existing P resources are limited (estimated to last for 170-890 years).[1–3] This makes recycling of P from crop residues and anthropogenic wastes to agricultural land an essential sustainability strategy that will help ensure continuing access to P for food security, and as a positive side effect reduce negative effects of P leaching into water bodies (algae blooms and eutrophication). Changes in legislation, e.g. in Germany, Switzerland and the EU, have increased the incentive and urgency of finding alternative ways of P recycling from waste materials, such as sewage sludge.[4–6]

Sewage sludge, a waste product from sewage treatment in waste water treatment plants, has agronomically relevant levels of N (1.5-4.0%), P (0.3-1.2%) and organic carbon[7] and therefore, it has been used as soil amendment on agricultural soils for centuries to maintain productivity.[8] However, application of untreated sewage sludge poses health risk concerns due to pathogens and organic and inorganic contaminants.[7] Emerging contaminants, such as pharmaceuticals, personal care products, flame retardants and microplastics have further increased the concern about the agricultural use of sewage sludge.[9–11] Processes, such as composting and anaerobic digestion can address these associated health concerns at best only partially.[11–13]

Thermal treatments, incineration and pyrolysis, are alternative processing methods. Pyrolysis is a thermo-chemical conversion process under oxygen-limited conditions. It sterilises the material and reduces the concentration of organic toxins (e.g. PAHs, PCBs and dioxins), pharmaceuticals (e.g. hormones) and other microconstituents (plastics, surfactants).[12–17] It

65 also immobilises potentially toxic elements (PTE) present in the feedstock, such as copper
66 (Cu), cadmium (Cd) and chromium (Cr), reducing risk of leaching and plant uptake.[18,19] In
67 contrast to incineration, pyrolysis retains most of the carbon present in sewage sludge and
68 even converts it into a recalcitrant form. Therefore, if pyrolysis vapours and liquids are used
69 to fuel the process or renewable energies, pyrolysis can be considered the most sustainable
70 treatment for sewage sludge from the perspective of atmospheric carbon removal and storage,
71 and environmental impacts.

72 Sewage sludge biochar, pyrolysed sewage sludge that is applied to soil, typically has levels of
73 potassium (K) of 0.2-1.7%,[20] rather low for use as agricultural fertiliser and can even sorb K
74 from soil.[21] Although most sewage sludge biochars and incineration ashes contain
75 agriculturally relevant levels of P (1.0-20%),[20,22] little P is mobile with the P availability
76 being lower than in the source material.[23–25] Slow-P-release fertiliser might be desired in
77 certain applications, yet, in modern agriculture, immediate and, most importantly, predictable
78 P release is needed. Since, the P availability in biochar is highly variable,[22] current biochars
79 are unsuitable as P-fertiliser and modification and optimisation of biochar is required.

80 Previously, it was shown that additions of Ca, Fe and Mg to biomass before pyrolysis can
81 decrease the P availability in biochar.[26] We anticipate that K-doping can do the opposite:
82 potassium phosphate salts demonstrate very high solubilities[27] and our hypothesis is that
83 pyrolysis could result in preferential formation of potassium phosphates if K is present in
84 excess increasing P availability in biochar. We used potassium acetate for biochar doping
85 since it is a common, low-cost salt (700-1000 USD t^{-1})[28] that is used for general applications
86 such as de-icing. The aim is to produce a more complete carbon sequestration-fertiliser
87 product with well-balanced availability of nutrients. Sewage sludge was doped with 2%
88 (weight %) and 5% K as prior to pyrolysis at 700°C and the nutrient and PTE availability,

location of P, K and Ca and P speciation in biochar was studied using extractions, synchrotron XRF mapping, and XANES.

Materials and Methods

Feedstock preparation and pyrolysis

The effect of the feedstock's K content on biochar yield and properties was tested by altering the K content in sewage sludge. Sewage sludge was used because it is anthropogenic waste material with high nutrient contents that needs treatment before soil application. The sewage sludge was provided by Scottish Water in an undigested, dried and granulated form.

As described previously,[29] an aqueous solution of potassium acetate was sprayed onto oven-dried sewage sludge to restore the original moisture content and add 2% and 5% w/w K to the dry feedstock materials. On the basis of previous experiments, we chose to dope sewage sludge with 2% and 5% K.

The 2% and 5% K-doped sewage sludge were pyrolysed using the continuous pyrolysis unit (auger reactor) at the UK Biochar Research Centre, University of Edinburgh. The pyrolysis unit is heated by an electric split-tube furnace (inner diameter 100 mm) and the feedstock residence time in the heated zone is around 21.5 min. Details about the unit and a schematic are published in Buss et al.[30]. Based on previous results and the availability of the 700°C sewage sludge biochar as Edinburgh Standard Biochar[31] (based on the same feedstock batch), a temperature of 700°C was chosen.

The undoped sewage sludge biochar used as a reference material here was produced using the pilot scale continuous pyrolysis unit of the UKBRC (details in Mašek et al.)[32]. We were able to show previously that key properties of the biochars produced in our two continuous pyrolysis units are not significantly different from each other.[32]

The materials are abbreviated as follows: SS, sewage sludge; SS 700, sewage sludge 700°C; SS 700 + 2% K, sewage sludge 700°C with 2% K; SS 700 + 5% K, sewage sludge 700°C with 5% K doping.

Thermogravimetric analysis (TGA)

A Mettler-Toledo TGA/DSC1 was used to perform pyrolysis followed by proximate analysis for accurate yield determination of the sewage sludge biochars.

Around 70-100 mg (one granule) undoped and K-doped sewage sludge was placed in a 150 µL alumina crucible. The following temperature profile was applied: drying at 110°C for 10 min, 90°C min^{-1} dynamic phase to heat to 700°C, static phase of 10 min matching the heating rate and residence time at the highest treatment temperature (HTT) of the continuous units.[32]

Subsequently, the biochar was ground up in the crucibles used for TGA-pyrolysis and a standard proximate analysis protocol was used in the TGA. During proximate analysis the biochar is heated up to 110°C in a nitrogen atmosphere to drive-off moisture, followed by heating to 900°C to determine the volatile mater content. Subsequent introduction of air oxidises the sample and the fixed carbon (FC) and ash content was determined. The equations used to calculate the yields and FC content can be found in Buss et al.[33]

Biochar characterisation

Sub-samples (typically at least 20-50% of the total biochar amount) of the doped and undoped biochars were ground up with mortar and pestle. Further sub-samples were taken, and following analyses performed.

Electric conductivity (EC) and pH

The biochars were extracted in glass vials with deionised (DI) water in a solid-to-liquid ratio of 1:20 according to Rajkovich et al.[34] The samples were shaken on an orbital shaker for 1.5

h at 150 rpm and subsequently analysed with a Hach HQ40d portable meter using a Hach conductivity probe CDC 401 and a sension gel-filled pH-electrode Hach 51935-00.

Extractions and digestions

The biochars were digested using modified dry ashing with a combination of HNO_3 and H_2O_2 and dry ashing at 500°C for 8 h.[35] More details and modifications to the original method can be found in Buss et al.[30]

Different extraction methods were applied to characterise the availability of nutrients and PTEs in biochar. Extraction with 0.01 M $CaCl_2$ was identified as the best extraction technique for available P in Shepherd et al.[36] In addition, DI water extraction was chosen and a formic acid (FA) extraction, which also showed good correlation with plant P uptake in Shepherd et al. and Wang et al.[36,37]

The extraction protocol for the $CaCl_2$ and water extraction was the following: 1.5 g ground biochar was extracted with 15 mL solution in 50 mL polypropylene centrifuge tubes. The tubes were shaken on an orbital shaker for 2 h at 150 rpm. Subsequently, the samples were filtered with Whatman No. 1 filter paper. Blanks were added and triplicate extractions conducted, respectively.

The formic acid extraction was performed according to Shepherd et al.[36]: 200 mg of biochar was weighted into 50 mL centrifuge tubes in triplicates and 20 mL 2% FA was added. Reagent blanks were prepared, and the samples were shaken for 2 h at 150 rpm and filtered with Whatman No. 1.

The digests and extracts were analysed via inductively coupled plasma optical emission spectroscopy (ICP-OES) as described in section 2.3.4. The % available of the total elemental content was calculated.

Repeated water extraction (Edinburgh Biochar Toolkit D)

As described in Buss et al.,[38] 5 g biochar and sewage sludge were extracted with DI water and 0.05 M 2-ocatanol (non-ionic surfactant to mitigate any short-term hydrophobic effects of biochar). The experiment was performed in glass bottles, which were shaken at 150 rpm for 1.5 h. After filtering, the solution was analysed for P via ICP-OES. The biochar was extracted again with the same DI water-to-surfactant ratio. The experiment was repeated six times in triplicates (extraction step 3, 4, 5 and 6 with 2% and 5% K-amended biochars only performed in duplicates).

The accumulated percentage elemental extractability was gives as averages with standard deviation (error propagation was applied).

Elemental analysis

All extracts and digests were analysed by ICP-OES (Varian Vista Pro) for Al, Ca, Mg, K, P, Fe, Mn, Zn, and Cu (As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn in the Supplementary Information) using calibrations from 0.01 to 25 ppm. Detailed descriptions of the ICP-OES procedure and data processing can be found in Buss et al.[30]

Mineralogical composition of sewage sludge samples

Biochar samples were ground up and sieved to a fraction size below 0.063 mm. X-ray diffraction (XRD) was used to characterise the crystalline phases present in the sewage sludge samples. A Bruker D8 advance XRD instrument with a Cu Anode was used at 40 mA and 40 kV with a NaI detector, which analysed at 6 s/step from 2 to 65° in 0.025°/step increments. The raw data were evaluated with the software TOPAS 3.0 Rietveld. The biochar samples were spiked with 20% calcite to quantitatively measure the composition of mineral in the samples relative to a known concentration of calcite.

Synchrotron X-ray analysis of P-species in biochar

The P distribution and speciation in the dehydrated SS 700 and SS 700 + 5% K biochars were investigated by X-ray fluorescence (XRF) elemental mapping and X-ray absorption near edge spectroscopy (XANES) at the I18 beam line at Diamond Light Source (UK) using a monochromator with Si(111) crystals and a helium-purged sample chamber to reduce X-ray attenuation.

X-ray fluorescence (XRF) elemental mapping

The spherical particles of biochars were cut and placed onto Kapton tape. The XRF elemental mapping was run on the dehydrated SS 700 and SS 700 + 5% K biochar particles with a resolution of 2-3 μm in order to investigate the P distribution and association of P with Ca and K in the samples.

X-ray absorption near edge spectroscopy (XANES)

P K-edge XANES measurements of particular phases enriched with P and average P spectra were collected in order to examine the P speciation in the dehydrated SS 700 and SS 700 + 5% K biochars. The reference materials of P-containing compounds of analytical quality reagents (Sigma-Aldrich) selected for the XANES analysis were: hydroxyapatite ($Ca_5(PO_4)_3(OH)$), calcium phosphate ($Ca_3(PO_4)_2$), calcium phosphate dibasic ($CaHPO_4$), calcium phosphate monobasic ($Ca(H_2PO_4)_2$), potassium phosphate (K_3PO_4), potassium phosphate monobasic (H_2KPO_4), potassium phosphate dibasic (K_2HPO_4), iron (III) phosphate dihydrate ($FePO_4 \cdot 2H_2O$), aluminium phosphate ($AlPO_4$). The reference material spectra were recorded in transmission mode using an ionization chamber. The sample spectra were recorded in fluorescence mode using a 4-element energy-dispersive fluorescence detector.

Data analysis and statistics

The data were tested for normality with a Shapiro-Wilk test before conducting one-way ANOVA with SigmaPlot 11 followed by Student-Newman-Keuls pairwise post hoc comparison test. The data set from single-step and repeated water extraction of P failed the Shapiro-Wilk test. Yet, one-way ANOVAs are robust against violation of the normality assumption.[39]

The XANES spectral analysis was performed using Athena.[40] Linear combination fitting (LCF) of the spectra for P in the dehydrated SS 700 and SS 700 + 5% K biochars with those of the reference materials was performed in derivative space, to identify P species that were present in the investigated samples.

Results and Discussion

Elevated phosphorus (P) and potassium (K) availability

The extractable P content in untreated sewage sludge was low, only 1.5% and 1.2% of the total P was extracted with 0.01 M $CaCl_2$ and water, respectively; formic acid (FA) extracted 16% of the total P (Figure 1, Table 1). After pyrolysis at 700°C, the P availability was even lower, $CaCl_2$ extracted <0.01% of the total P, water 0.04% and FA 2.9%. In Zhang et al.[22], no P was water-extractable in sewage sludge biochar produced >400°C supporting our results.

Doping of sewage sludge with K successfully increased the water-extractable of the total P content in the one-step extractions from 0.04% in the undoped biochar to 3.0% and 8.7% with 2% and 5% K addition, respectively; an increase by 81 and 237 times (Figure 1). In addition, the treatment increased the 0.01 M $CaCl_2$ and the FA extractable P (Table 1). Repeated water extractions (Edinburgh Tool Kit D), simulating P release over time, continued to extract P (Figure S1-Sn). At the end of sixth extraction steps, 7% and 16% of the total P was extracted in the 2% and 5% K-amended biochar, respectively, compared to only 0.4% and 3% in the SS 700 and untreated sewage sludge (Figure 1). In the 5% K-amended biochar, the same amount of P was extracted with FA in one extraction step as with water in 6 extraction steps.

The total K concentration in sewage sludge was around 10 times lower than the concentration of P, which is not unusual for sewage sludge samples.[21,41] In the undoped sewage sludge biochar, water extracted only low amounts of K (Table 1). The addition of K prior to pyrolysis increased the extractable fraction of K ($CaCl_2$ and water) to 30-50% of the total K content in a single extraction step (Table 1). Repeated water extraction resulted in 100% recovery of the total K content in the two amended biochars (Table 1, Figure S1-Sn). High amounts of K immediately available to plants can cause localised toxic effects and low nutrient-use efficiency due to K leaching through soil, an issue observed for biochar and

237 combustion ashes.[23,42] Therefore, initial availability of 1/3 to 1/2 of the K but eventually full
238 accessibility of the K in the enhanced biochar could be a good balance but needs to be
239 confirmed in plant trials. Overall, the results are very promising for K-enhanced sewage
240 sludge biochar to be used as P and K fertiliser.

241 K-doping changes P speciation in biochar

242 Extractability of P binding partners

243 Elements such as Ca, Mg, Al and Fe bind to P to form minerals of low solubility[27] that limit P
244 mobility and plant uptake in soil and biochar.[43–45] Sorption of P to Al, Ca, Mg and Fe is also
245 the main mechanism responsible for P retention by biochar.[46] Changes in extractability of P
246 binding partners in sewage sludge after pyrolysis and with K-doping can be evidence for a
247 change in P speciation.

248 The extractability of Ca, Mg, Al and Fe undoped sewage sludge biochar was lower than in
249 the untreated sewage sludge (in all three extractants; Figure 2). The P in biochar feedstocks
250 from manure and plant residues is predominantly present in organic forms, e.g. in DNA and
251 phytate[47,48], while sewage sludge is mostly composed of inorganic, ortho-P.[44] Pyrolysis
252 converts a proportion of P in both types of material into P-containing minerals of low water-
253 solubility (Ca, Mg, Al and Fe phosphates)[25,44,45,47,48], reducing the extractability of both, P
254 and P-binding partners.

255 The hypothesis is that with K addition, instead of forming salts of low water-solubility,
256 during pyrolysis P binds preferentially to K to form salts of high water-solubility, such as
257 potassium dihydrogen phosphate (KH_2PO_4), potassium hydrogen phosphate (K_2HPO_4) and
258 potassium phosphate (K_3PO_4).[27] Ca, Mg, Al and Fe that typically bind to P in biochar instead
259 form other, more soluble compounds, increasing their extractability in the K-amended
260 biochar compared to the unamended biochar. This is indeed the case for most samples giving

261 evidence supporting our hypothesis (Figure 2). Yet, the concentration of Ca and Mg in the
262 water and $CaCl_2$ extracts was lower in the K-doped biochars compared to the undoped SS
263 700 (net decrease of Ca in Figure 3 is a result of subtracting Ca concentration in the blank
264 from the analyte).

265 Two different factors need to be considered that determine the concentration of P and Ca,
266 Mg, Al and Fe in the analyte: first the initial solubility of the biochar inherent minerals and
267 secondly, the solution conditions and composition as once dissolved P can precipitate over
268 time, e.g. with Ca, which then is not quantified by the detector. Formation and precipitation
269 of significant quantities of calcium phosphate is only possibly when high phosphate
270 concentrations are present in solution[49] as is the case in the 5% K doped biochar. The solution
271 pH in the water- and $CaCl_2$-extracts were close or slightly lower than the pH displayed in
272 Table 1 (pH ~10 for the amended biochars), which are suitable conditions for calcium
273 phosphate but not for aluminium and iron phosphate precipitation. Subsequently, with ample
274 P present in solution and a suitable pH for Ca and Mg-P precipitation, the Ca and Mg
275 concentration in the water and $CaCl_2$-extracts of the K-amended biochars was lower than in
276 the undoped biochar (less P present for precipitation) and sewage sludge sample (lower pH
277 unsuitable for precipitation).

278 In the 5% K-doped biochar, FA and water extracted the same amount of P in one and six
279 extraction steps, respectively (Table 1). In contrast, FA extracted nearly 10 times more P than
280 the water extractions in the SS 700 biochar as also shown in Zwetsloot et al.[50] This indicates
281 that the P in the doped sample is extracted regardless of the solution pH and type of
282 extractant, while specific conditions are necessary to extract the P from SS 700. This is
283 further proof that the P species have changed with K addition.

With pyrolysis the extractability of Ca, Mg, Al and Fe decreased due to conversion of organic to mineral P that form minerals with these P binding partners. While K addition prior to pyrolysis increased the water solubility of P binding partners in biochar, it also increased Ca and Mg precipitation (as phosphates) when extracted at the native biochar pH, hence limiting Ca, Mg and likely P availability. According to Barrow, in soils, calcium phosphate precipitation is not a factor that significantly contributes to P immobilisation.[49] Still, in certain soils (excess availability of Ca and Mg), a lower biochar pH (or biochar-soil solution pH) could further increase the immediate P availability. This is an important aspect to consider in design of biochar for specific soils and applications requiring controlled P delivery.

P-speciation analysed by XRD, Sy-XRF and XANES

We used Sy-XRF mapping to identify the location of Ca, K and P in biochar to track any changes with K-doping, Ca-P being the most common P-containing mineral at high pyrolysis temperatures.[45] The brown background of the interior of SS 700 biochar (Figure 3b) shows an even distribution of P and Ca, which likely associate with each other (red – P and green – Ca results in brown). In the K-amended biochar (Figure 3d) a purple ring enveloping the biochar centre is visible up to 200-300 µm from the biochar surface, clearly showing that K and P associate with each other (red – P and blue – K results in purple). The centre of the biochar particle is still coloured brown demonstrating that there are still significant amounts of Ca-P present in the centre. The existence of the ring of K is likely explained by the K not having fully penetrated to the biochar centre during initial doping. A more equal distribution of K during doping, e.g. through longer soaking in K-rich solution could further increase the K-P association and henceforth, P availability. This hypothesis will be tested in follow-up studies. The results demonstrate not only the feasibility of increasing the P availability, but also that further optimisation of K distribution for maximum P availability is viable.

309 We could neither identify distinct differences between the XRD spectra of the biochars
310 (Figure S2-Sn), nor any particular P crystalline phases. This indicates that most of the P
311 phases were amorphous or present in small concentrations of many different minerals, below
312 the level of detection. This was confirmed in Qian and Jiang, who did not identify any P
313 crystalline phases in sewage sludge biochar produced by pyrolysis at 400-700°C using XRD;
314 only stanfieldite ($Ca_4Mg_5(PO_4)_6$) was identified in biochar produced at 800°C.[44]

315 Therefore, we analysed SS 700 and the 5% K-doped biochar with P K-edge XANES in five
316 replicates enabling a higher resolution. The results of linear combination fitting (LCF)
317 (Figure 4) of three replicates of SS 700 (SS 700(1) – SS 700(3)) demonstrate that the spectra
318 mainly associated with aluminium phosphate ($AlPO_4$) with a dominant narrow peak at around
319 2152.5 eV (the P absorption edge) followed by a much broader peak at reference line (f). In
320 contrast, the spectra SS 700(4) and SS 700(5) mainly associated with the hydroxyapatite
321 ($Ca_5(PO_4)_3(OH)$) spectrum that has a dominant, much broader peak at around 2152.5 eV with
322 a pronounced shoulder at reference line (a) followed by two broad peaks at around lines (c)
323 and (e) (Figure 4). Results from linear combination fitting of the P K-edge XANES spectra
324 for sewage sludge biochars confirm the occurrence of $AlPO_4$ and $Ca_5(PO_4)_3(OH)$ (Table S1-
325 Sn). Both compounds were also identified as key P-containing compounds in Sun et al.[51]
326 Hydroxyapatite and aluminium phosphate are both poorly soluble P compounds with
327 solubility products of 3.04×10^{-59} for ($Ca_5(PO_4)_3(OH)$) and 6.3×10^{-19} for $AlPO_4$ explaining the
328 low solubility of P in SS 700 (Figure 1).[52]

329 The LCF results indicate that hydroxyapatite and aluminium phosphate are still present in the
330 5% K-doped biochar, however, in addition K_2HPO_4, highly water soluble (168 g/100 g
331 H_2O[27]), appeared in the modified biochar (Table S1-Sn). The K_2HPO_4 spectrum has a
332 dominant narrow peak at 2152.5 eV with a broad post-edge shoulder at line (b) followed by a
333 much broader peak at line (d) (Figure 4). The LCF of the spectra for P in the 5% K-doped

biochar (replicates 3-5) shows residues and not a good correlation fit with the tested reference materials that can indicate the presence of other P-bearing phases that were not covered by used reference materials.

In summary, our results demonstrate that with addition of K before pyrolysis P-minerals of very high solubility, such as potassium hydrogen phosphates, were formed confirming our hypothesis that P availability can be modified and customised with simple and cost-effective mineral additions.

Carbon sequestration potential of doped biochar

Besides agronomically relevant levels of nutrients, sewage sludge biochar contains stable carbon and when applied to soil, can sequester atmospheric carbon dioxide for centuries [53]. Therefore, we tested the biochar yield and the yield of fixed carbon (FC) as influenced by K addition, FC being a proxy for what remains in soil after ~100 years.[54–56]

The biochar yield of sewage sludge (in % of dry feedstock) was 37.6%, which increased to 39.4 and 39.9% with the addition of 2% and 5% K, respectively (Table 1). The FC yield per feedstock and per ash-free feedstock input both increased by around 20% and 10% with 2% and 5% K, respectively (in relative terms, Table 1) (see more details on calculation and interpretation in Buss et al.[33]). Therefore, 2% K-doping maximises the carbon sequestration potential of sewage sludge biochar.

Previously, we demonstrated that 2% K-doping boosted the carbon sequestration potential of *Miscanthus* biochar by 45% due to catalytic effects of alkali (and earth alkaline) metals, which increase biochar formation and yield.[29] The sewage sludge in our current study had a 5 times higher concentration of inherent alkali and earth alkaline metals (1.5% K, Ca and Mg; Table S1-Sn) than the *Miscanthus* biomass (0.3% K, Ca and Mg; unpublished data). Therefore, the addition of 2% K had a smaller effect on overall alkali and earth alkaline metal

content in sewage sludge compared to the content in *Miscanthus*, likely resulting in less catalytic effects and biochar yield increases.

In Buss et al. blending of pine biomass with wood ash, rich in alkali and earth alkaline metals, increased the FC yield (ash-free feedstock) significantly and the highest wood ash addition had the strongest effect.[33] In our current study, 2% K performed better in terms of FC yield than 5% K-doping (Table 1) demonstrating there is an optimum K addition for maximum FC yield. This is a significant finding and highlights the need to investigate different feedstocks separately and tailor the biochar-mineral formulation individually to maximise the carbon sequestration potential.

Sewage sludge biochar fertiliser in agriculture

The P content in the biochar under investigation (2%) is low for biochar produced from sewage sludge, which can have P contents of 6-20%, more P than present in refined super-P fertiliser.[18,22,41] In our study, water and FA both extracted 16% of the total P in six and one extraction step, respectively. Assuming an average sewage sludge biochar P content of 10%[18,22,41] and a P availability of 16%, in total 1.6% of the biochar would likely be immediately plant-available P. At a P application rate of 40 kg ha^{-1}, ~2.5 t ha^{-1} of biochar would satisfy the typical P demand of wheat (winter wheat).[57] In addition to the immediately available P, this amendment adds extra P to the soil that can be used in future growing cycles.

Application of 2.5 t ha^{-1} of a sewage sludge biochar with the same composition as the one in our study would also supply ~95 kg K ha^{-1} (demand for winter wheat ~133 kg K ha^{-1}).[57] More K could be added to the sewage sludge to make even more P available and to provide enough K for specific crops, depending on application. In addition, such biochar fertiliser (in 2.5 t ha^{-1}) sequesters 445 kg ha^{-1} of carbon likely stable for >100 years (fixed carbon dry basis in Table 1), supply micronutrients, such as Ca, Mg, B, Mn and Mo (Table S1-Sn) and increase

382 the pH of acidic soil (pH 10.77; Table 1). The effect of sewage sludge biochar on soil pH was
383 demonstrated in Buss et al.[58]. Therefore, K-amended biochar can be a great multi-functional,
384 environmentally sustainable fertiliser.

385 An often raised concern regarding application of sewage sludge in agriculture is its levels of
386 potentially toxic elements (PTEs),[14,59] which are enriched in biochar due to decomposition
387 and volatilisation of a proportion of the organic matter during pyrolysis, while the PTEs
388 remain.[30] Yet, the availability of PTEs drastically decreased after sewage sludge pyrolysis, in
389 both, undoped and doped-biochar (Table S2), e.g. the water-extractable contents of Cu, Ni
390 and Zn were all reduced by 82-93% after pyrolysis of 5% K-amended sewage sludge.
391 Therefore, as concluded by other authors, in terms of PTE toxicity sewage sludge biochar
392 application in agriculture is likely to be much safer than the still widely practiced application
393 of unpyrolysed sewage sludge.[18,42,60] Importantly, pyrolysis destroys a whole suite of organic
394 contaminants present in sewage sludge resulting in markedly increased safety.[12–17]

395 To further optimise (sewage sludge) biochar as a fertiliser, refinement of the method
396 presented here is possible, e.g. through change in biochar pH, feedstock K/P ratio,
397 concentration and form of K minerals and K distribution in the feedstock (soaking time). This
398 new class of fertiliser contributes to nutrient recycling and reduced nutrient leaching, reduces
399 the dependence on fertiliser imports (as intended as part of the new fertiliser regulation in the
400 EU[6]) and helps to comply with new circular economy legislation, e.g. the German and Swiss
401 legislation on P recycling from wastewater.[4,5]

402 Conclusions

403 Sewage sludge-based biochar fertilisers offer a number of advantages compared to synthetic
404 fertilisers, namely they are produced from sustainable resources, improve soil properties and
405 store carbon. However, to be able to replace synthetic fertilisers in conventional farming

406 systems, it is essential for biochar-based fertilisers to have a predictable and consistent
407 release of nutrients. In this study, potassium acetate addition in low concentrations (5%)
408 before pyrolysis increased the water-extractable P content in biochar by several orders of
409 magnitude over the undoped biochar. In addition, it significantly increased the 2% formic
410 acid and 0.01 M $CaCl_2$ extractable P and the P extracted after six water extraction steps. The
411 results from this study open up a new, simple way to modify and hence, control the P
412 availability in biochar using a low-cost K additive, yielding a new class of PK fertiliser. Our
413 new multifaceted approach links waste management, soil management and food production in
414 a virtuous cycle fully aligned with the circular economy and zero-waste concepts.

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417 analysis, respectively. This work was carried out with the support of the Diamond Light
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419 provision of the sewage sludge feedstock.

420 Supporting Information

421 Results for repeated water extraction for P and K, an XRD spectra of the biochars and tables
422 showing results from P K-edge XANES and elemental analyses of the biochars.

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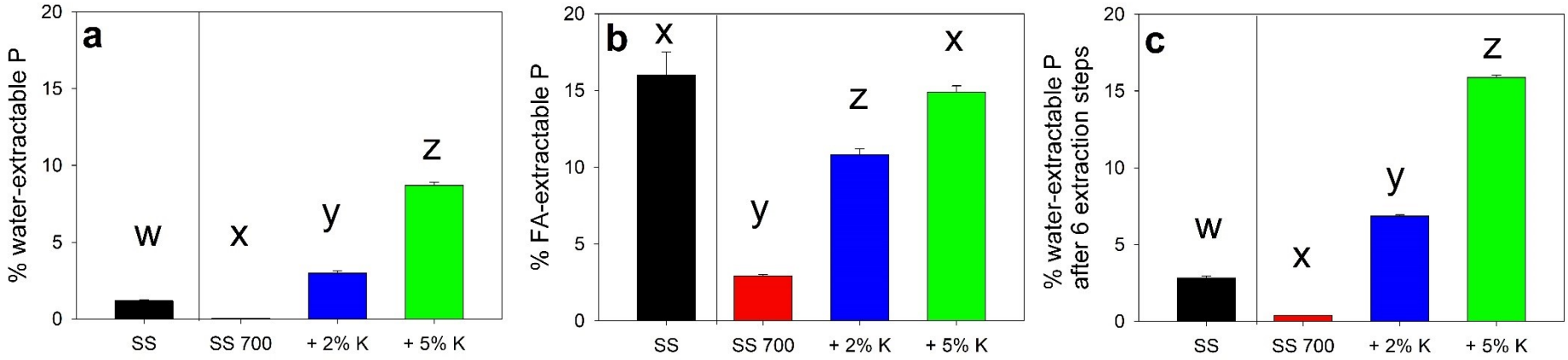
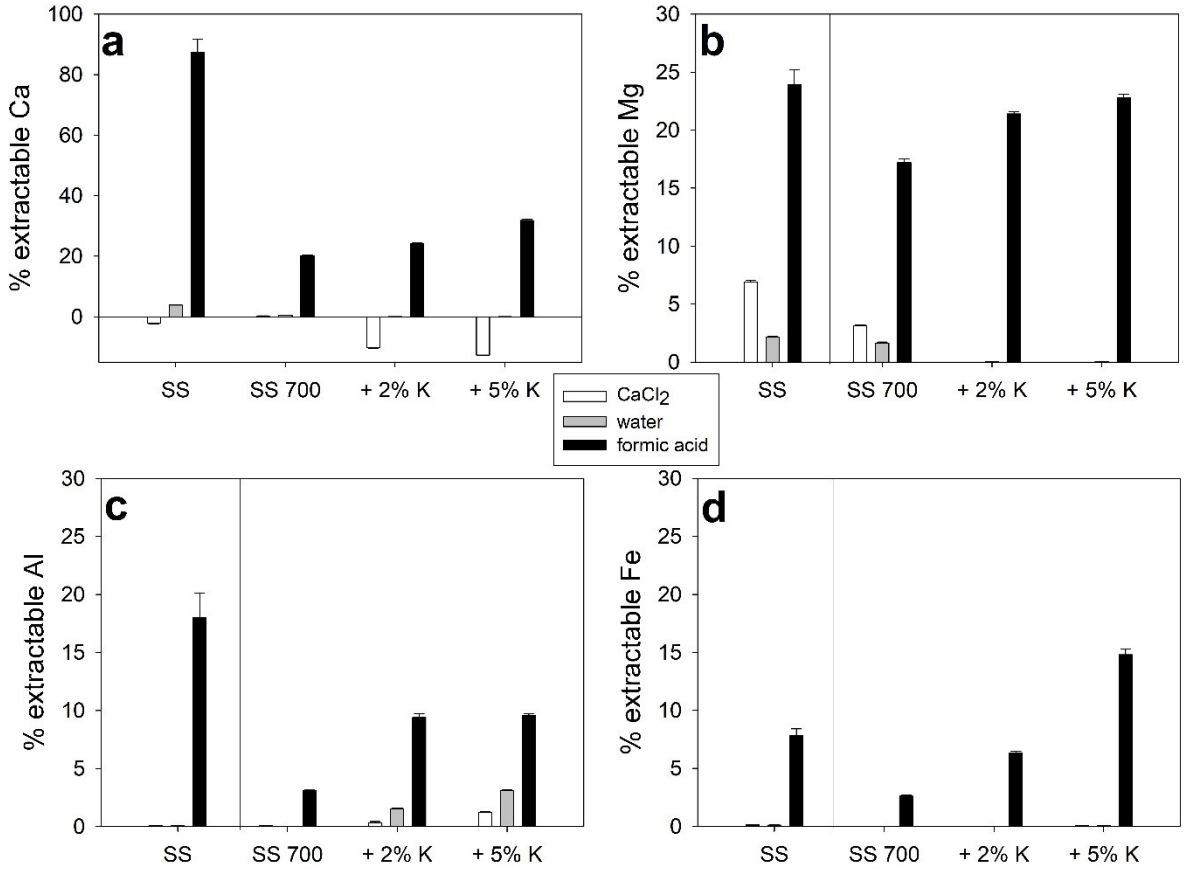


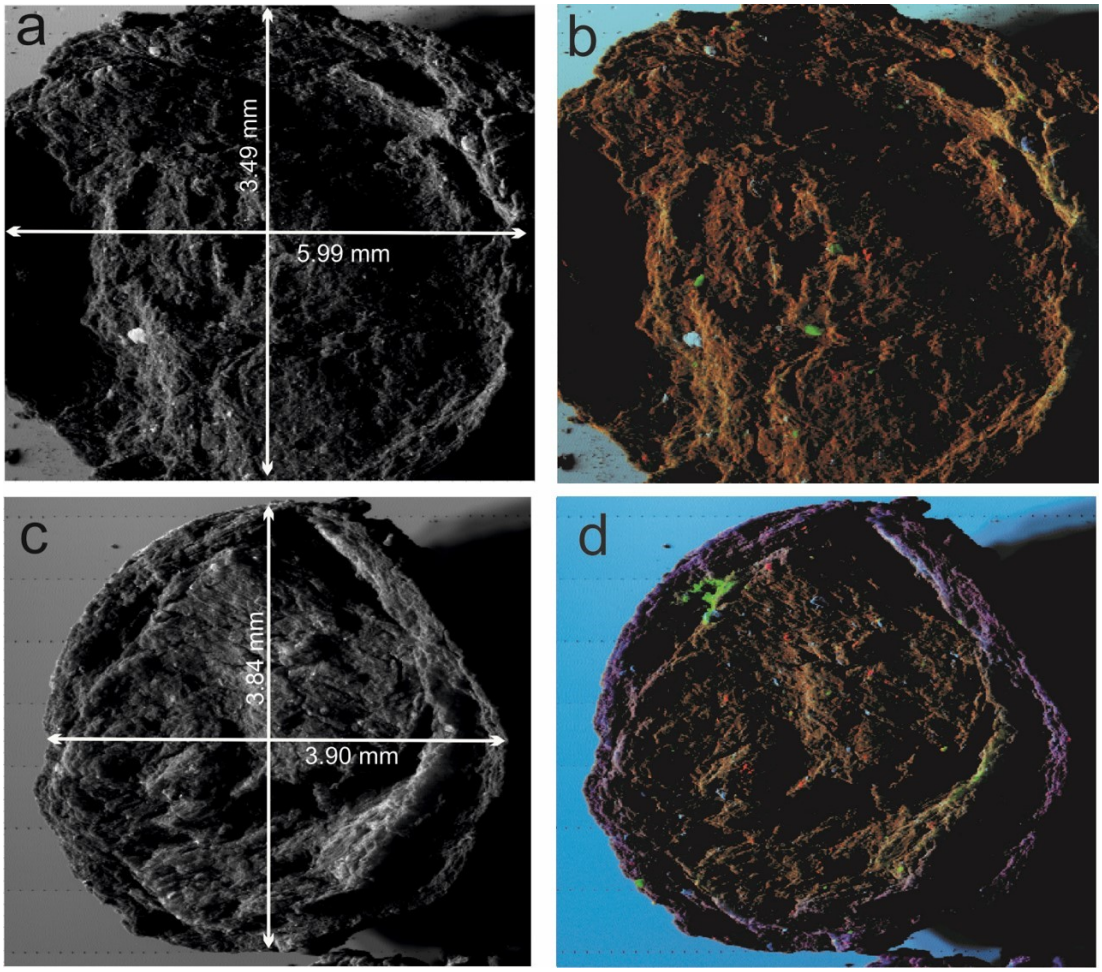
620

621 Figure 1: (a) Water- and (b) formic acid (FA)-extractable P content as % of the total content in sewage sludge (SS) and sewage sludge biochar.
622 Panel (c) shows the P concentrations from biochar extracted in 6 extraction steps (Edinburgh Toolkit D). Biochar was produced at 700°C
623 without addition (SS 700) and with 2% and 5% K addition prior to pyrolysis. Mean and standard deviation of three replicates are shown. Letters
624 show significant differences among the treatments ($p < 0.05$, one-way ANOVA).



625

626 Figure 2: Percentage water-, 0.01 M $CaCl_2$- and formic acid-extractable (a) Ca, (b) Mg, (c) Al
627 and (d) Fe content as % of the total content in sewage sludge (SS) and sewage sludge biochar.
628 Biochar was produced at 700°C without addition (SS 700) and with 2% and 5% K addition
629 prior to pyrolysis. Mean and standard deviation of three replicates are shown.

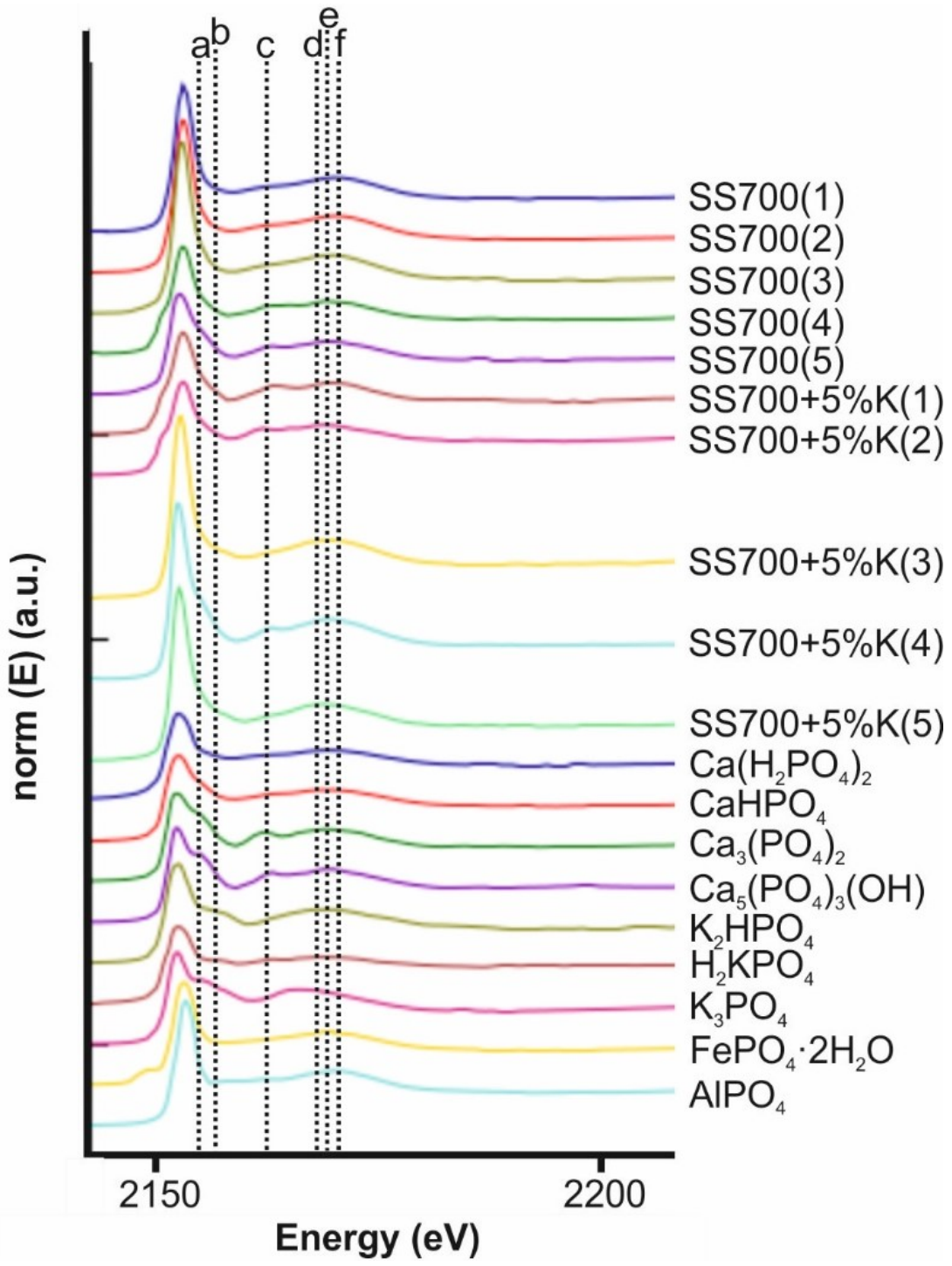


630

631 Figure 3: Picture a-d are images of the internal view of the biochar spherical particles (a: SS

632 700; c: SS 700 + 5% K) and the synchrotron-XRF maps (b: SS 700; d: SS 700 + 5% K) with

633 P – red, Ca – green, K – blue.



634

635 Figure 4: Phosphorus K-edge XANES spectra of sewage sludge biochars with 5% K addition
636 prior to pyrolysis (SS 700 + 5% K) and without (SS 700) produced at 700°C in five replicates
637 ((1) - (5)). In addition, reference materials of P-containing compounds likely present in
638 sewage sludge (biochar) are shown. The dotted lines and letters are references indicating
639 energy levels that characterise unique spectral features for different P species.

640 Table 1: Properties of sewage sludge (SS) and sewage sludge biochar produced at 700°C
641 without addition (SS 700) and with 2% and 5% K addition prior to pyrolysis. FC, fixed
642 carbon; EC, electric conductivity. In most cases mean and standard deviation of three
643 replicates shown. Yield and proximate analysis results are on dry basis. Different numbers
644 indicate statistical differences among the treatments. [#] not tested: for proximate analysis, only
645 the biochars, not the feedstock, were compared with each other statistically, as appropriate.

		SS	SS 700	+ 2% K	+ 5% K
yield					
biochar yield	% feedstock	-	37.62 ± 0.37a	39.40 ± 0.09b	39.88 ± 0.22b
ash-free biochar yield	% feedstock	-	12.17 ± 0.21a	13.40 ± 0.04b	13.59 ± 0.07b
ash-free biochar yield	% ash-free feedstock	-	16.33 ± 0.31a	18.11 ± 0.06b	18.44 ± 0.12b
FC yield	% feedstock	-	6.44 ± 0.16a	7.66 ± 0.08b	7.10 ± 0.12c
FC yield	% ash-free feedstock	-	8.64 ± 0.19a	10.34 ± 0.10b	9.63 ± 0.14c
proximate analysis					
volatile matter	% ash-free	89.4 ± 0.4[#]	47.1 ± 2.1a	42.9 ± 0.5b	47.7 ± 1.1a
FC	% ash-free	10.6 ± 0.3[#]	52.9 ± 2.1a	57.1 ± 0.5b	52.3 ± 1.1a
FC	% dry	17.1 ± 0.6[#]	17.1 ± 0.6a	19.4 ± 0.2b	17.8 ± 0.4a
ash	% dry	27.7 ± 0.5[#]	67.6 ± 0.3a	66.0 ± 0.1b	65.9 ± 0.1a
pH		6.36 ± 0.10	9.60 ± 0.33	10.46 ± 0.12	10.77 ± 0.11
EC	µS cm^{-1}	368 ± 11	162.6 ± 17.8	1134 ± 158	2575 ± 455
K concentration					
total	mg kg^{-1}	1157 ± 42	3277 ± 35	23316 ± 284	37845 ± 320
$CaCl_2$	mg kg^{-1}	239 ± 3	23 ± 1.6	7135 ± 746	13580 ± 240
water	mg kg^{-1}	206 ± 5	32 ± 0.5	6984 ± 352	13471 ± 80
water-6 days	mg kg^{-1}	621 ± 15	140 ± 1.1	26059 ± 2823	41161 ± 3066
P concentration					
total	mg kg^{-1}	10984 ± 354	20309 ± 734	18965 ± 594	19555 ± 265
$CaCl_2$	mg kg^{-1}	166 ± 2.3	1.1 ± 0.3	< 0.26	340 ± 19
water	mg kg^{-1}	129 ± 7.0	9.6 ± 0.5	564 ± 21	1700 ± 35
water-6 days	mg kg^{-1}	311 ± 7.8	75 ± 1.2	1300 ± 10	3106 ± 17
formic acid (FA)	mg kg^{-1}	1756 ± 151	592 ± 11	2055 ± 29	2920 ± 71

646